REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
27-07-2012	Final Report	1-Apr-2009 - 31-Mar-2012

4. TITLE AND SUBTITLE
New Metal-organic Polymers Through Subcomponent Self-Assembly: Final Report

5a. CONTRACT NUMBER
W911NF-09-1-0110

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Jonathan R. Nitschke

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Cambridge
Department of Chemistry
University of Cambridge
CB2 1 -EW

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
54642-CH.6

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
ARO support has enabled the development of a new type of functional metal-containing polymeric material. Our key innovation has been to shift complexity away from devices, which are challenging to fabricate, and into molecules, which are challenging to synthesize. An understanding of self-assembly rules can then be used shift intellectual effort away from designing individual molecules and towards the design of systems that can self assemble to express a desired function. This approach is detailed in the attached late draft manuscript, soon to be

15. SUBJECT TERMS
supramolecular chemistry, polymers, luminescent materials, dynamic covalent chemistry

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jonathan Nitschke
UU	UU	UU	UU		19b. TELEPHONE NUMBER 004-412-2333

Report Title

New Metal-organic Polymers Through Subcomponent Self-Assembly: Final Report

ABSTRACT

ARO support has enabled the development of a new type of functional metal-containing polymeric material. Our key innovation has been to shift complexity away from devices, which are challenging to fabricate, and into molecules, which are challenging to synthesize. An understanding of self-assembly rules can then be used shift intellectual effort away from designing individual molecules and towards the design of systems that can self assemble to express a desired function. This approach is detailed in the attached late draft manuscript, soon to be submitted to J. Am. Chem. Soc.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
2012/07/25 1(4	Jack K. Clegg, Jonathan R. Nitschke, Wenjing Meng. Transformative Binding and Release of Gold Guests from a Self-Assembled Cu8L4 Tube, Angewandte Chemie International Edition, (02 2012): 1881. doi: 10.1002/anie.201108450

TOTAL: 1

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Smart Molecules Graduate Summer School, Leipzig (Germany), 6/2012
2. Cram Lehn Pedersen Plenary Lecture, International Symposium on Macrocyclic and Supramolecular Chemistry, Otago (New Zealand), 1/2012
3. Dalton European/African Lecture at the RSC Supramolecular and Macrocyclic Chemistry Meeting, Bath (UK), 12/2011
4. Anglo-German Conference on Inorganic Chemistry, Heidelberg (Germany), 9/2011
5. Keynote Lecture, International Symposium on Macrocyclic and Supramolecular Chemistry, Brighton (UK), 7/2011
6. Physical Organic Chemistry Gordon Conference, Salve Regina University (USA), 7/2011
7. British-German Frontiers of Science Symposium, Kavli Royal Society Centre, North Buckinghamshire (UK), 5/2011
8. European Supramolecular Science and Technology Group Meeting, Taormina (Italy), 10/2010
9. RSC Coordination Chemistry Discussion Group Meeting, Bath (UK), 7/2010
10. Keynote Lecture for the 'Frontiers of Supramolecular Chemistry' symposium of the Chinese Chemical Society meeting, Xiamen, 5/2010
11. Journées André Collet de la Chiralité, Dinard (France), 10/2009
12. Summer School of Nano Biology, Karlsruhe (Germany), 9/2009
13. Chemistry of Supramolecules and Assemblies Gordon Conference, Colby College (USA), 7/2009
14. Southampton Supramolecular Chemistry Symposium, University of Southampton (UK), 7/2009
15. International Symposium on Macrocyclic and Supramolecular Chemistry, Maastricht (Netherlands), 6/2009
16. Irvine Review Lecture, University of St Andrews (UK), 4/2009

Number of Presentations: 16.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper	
2012/07/25 1	5	Xavier de Hatten, Demet Asil, Richard Friend, Jonathan R. Nitschke. Aqueous Self-assembly of an Electroluminescent Double-helical Metallo-polymer, Journal of the American Chemical Society (07 2011)
2010/12/27 1	2	Xavier de Hatten, Nicholas Bell, Nataliya Yufa, Gabriel Christmann, Jonathan R. Nitschke. A Dynamic-covalent, Luminescent Metallopolymer that Undergoes Sol-to-gel Transition on Temperature Rise, (12 2010)

TOTAL: **2**

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

1. Cram Lehn Pedersen Prize in supramolecular chemistry, presented annually to a chemist worldwide within 10 years of the PhD, awarded 2/2012.

2. Dalton Transactions European/African Lectureship, presented annually to an inorganic chemist within 12 years of the PhD working in Europe or Africa, awarded 12/2011.

3. Corday-Morgan Prize, the top Royal Society of Chemistry prize for UK-based researchers under the age of 40, awarded 11/2011.

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Wenjing Meng	0.75	
FTE Equivalent:	**0.75**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Xavier de Hatten	0.25
FTE Equivalent:	**0.25**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Jonathan Nitschke	0.01	
FTE Equivalent:	**0.01**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Veerasak Srisuknimit	1.00	Chemistry
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Sean Houghton
William Taylor
Craig Woodhead
Sheng Hu
Total Number: **4**

Names of personnel receiving PHDs

NAME
Wenjing Meng
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

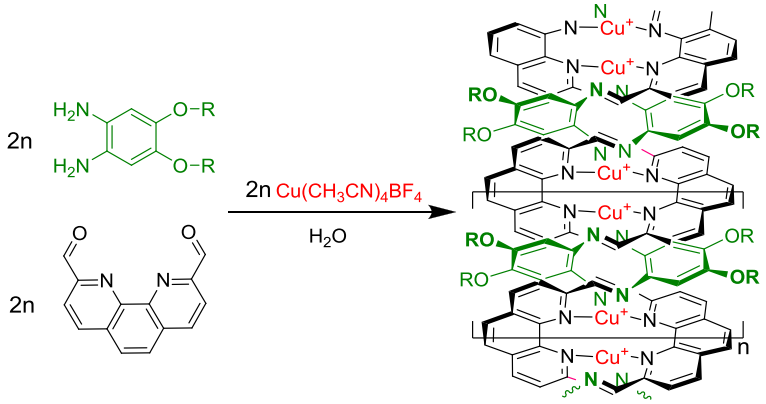
Dr Jonathan R. Nitschke
Department of Chemistry, University of Cambridge

Statement of the Problem Studied:

This project sought to synthesize and study the functions of new metallo-polymers prepared using the technique of *subcomponent self-assembly*. Two main subprojects validated our strategy, as described below.

Subproject A:

This project resulted in the creation of water soluble metal-containing polymeric material using subcomponent self-assembly. We developed the synthesis of double helical polymeric species according to the general procedure depicted in Scheme 1.



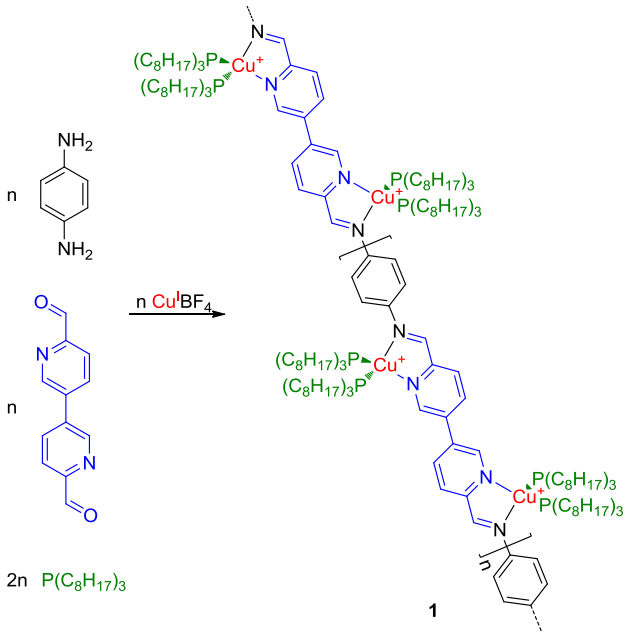
Scheme 1. Proposed synthetic path for the creation of water soluble metal containing polymers with a double helical shape

The polymers of Subproject A proved to be white-light emitters when built into devices in collaboration with the group of Richard Friend in the Cambridge Physics Department. These devices are described in the attached draft manuscript titled 'Aqueous Self-assembly of an Electroluminescent Double-helical Metallo-polymer', to be submitted shortly to the *Journal of the American Chemical Society*.

Subproject B:

In a second part of the project we have investigated the use of linear diamine and dialdehyde subcomponents to prepare rigid, linear polymers. Sterically hindered ancillary ligands such as trioctyl phosphine (TOP) were added to the copper coordination sphere in order to cap the vacant coordination sites, thus inhibiting crosslink formation and forcing linear growth by steric hindrance. The subcomponents used for this purpose are 1,4-phenylenediamine, 3,3'-bipyridine 4,4'-dicarboxaldehyde, copper(I) and TOP in DMSO as depicted in Scheme 2.

Dr Jonathan R. Nitschke
Department of Chemistry, University of Cambridge



Scheme 2. The preparation of conjugated metal-organic polymer **1**.

This polymer displayed a novel tendency to gel its solvent at high temperature, whereas most gel-forming polymers do so as the temperature is lowered. This work was reported in 'A dynamic-covalent, luminescent metallopolymer that undergoes sol-to-gel transition on temperature rise', X. de Hatten, N. Bell, N. Yufa, G. Christmann, J.R. Nitschke, *J. Am. Chem. Soc.* **2011**, *133*, 3158-3164, a reprint of which is included with this report.

Two of our key initial project goals have thus been met: we have validated the use of subcomponent self-assembly in the formation of metal-containing polymers, and these polymers have been shown to display novel and useful properties. Our key innovation has been to shift complexity away from devices, which are challenging to fabricate, towards molecules, which are challenging to synthesize. Our understanding of self-assembly rules can then be used shift intellectual effort away from designing individual molecules and towards the design of systems that can self assemble to express a desired function.

Other work:

Wenjing Meng, a PhD student who has just graduated and who was partially supported through this ARO grant, worked on several lines of enquiry described in the initial grant proposal, which ultimately did not prove fruitful. These consisted mostly in trying to use α,β-diketones as subcomponents for polymers. She then shifted her efforts to other projects, funded by the European Research Council. Because the first part of her studies in Cambridge was funded by this grant, ARO support has been acknowledged also on the following publications:

"Transformative Binding and Release of Gold Guests from a Self-Assembled Cu_8L_4 Tube", Wenjing Meng, Jack K. Clegg and Jonathan R. Nitschke, *Angew. Chem. Int. Ed.*, **2012**, 51, 1881-1884.

"A self-assembled M_8L_6 cubic cage that selectively encapsulates large aromatic guests", W. Meng, B. Breiner, K. Rissanen, J.D. Thoburn, J.K. Clegg and J.R. Nitschke, *Angew. Chem. Int. Ed.* ***2011***,

50, 3479-3483. **Featured on the inside front cover** of *Angew. Chem. Int. Ed.* **2008**, *50* (15). **Highlighted** in *Chem. Eng. News* **2011**, *89*, 41-42.

I remain very grateful to the Army Research Office's division of Basic Research for providing seed funding to allow this strand of research to take off within my group.